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(54) METHOD FOR PREPARING BATTERY COMPOSITE MATERIAL

VERFAHREN ZUR HERSTELLUNG EINES BATTERIEVERBUNDMATERIALS

PROCÉDÉ PERMETTANT DE PRÉPARER UN MATÉRIAU COMPOSITE DE BATTERIE

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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a preparation method, and more particularly to a preparation method of battery composite material and a precursor thereof.

BACKGROUND

[0002] Due to the sustained global energy shortage, the price of oil becomes higher and the environmental consciousness rises day by days. The most popular subject of the energy industry is how to provide a clean and effective energy. In a variety of alternative energies, the chemical battery is the most actively developing technology. With continued investment in research and development of related industries, the chemical battery technology is not only continuously improved and enhanced, but also widely used in our daily life, such as consuming electronics, medical equipment, electric bicycles, electric motorcycles, electric cars and electric buses.

[0003] Particularly, the Lithium Ferric Phosphate ($LiFePO_4$, hereinafter referred as "LFP") composite batteries are widely accepted by the market because of the large current and long life cycle. Also, the LFP composite batteries have no risk of explosion and have the advantages of high power efficiency and low pollution so as to be used in replace of the conventional lead-acid, nickel-metal hydride and nickel-cadmium batteries. After years of research, the Lithium Ferric Phosphate Nano-Co-crystalline Olivine (hereinafter referred as "LFP-NCO") battery is developed. The LFP-NCO battery is a single compound consisting Li, Fe, P and metals or precursor of metal composition, and is a non-coated and non-doped material, so that the LFP-NCO battery can significantly improve the power conductivity and eliminate impurities. Moreover, the price of the LFP-NCO battery is lower than conventional lithium ferric phosphate materials, in which the LFP-NCO battery has higher market competitiveness and becomes the main product of the industry.

[0004] In general, ferric phosphate ($FePO_4$), lithium hydroxide (LiOH) and lithium carbonate (Li_2CO_3) are applied to process a reaction of the conventional preparation method of LFP-NCO. Due to the high cost of raw materials of lithium hydroxide, the high requirement of much more ferric phosphate, and much more grinding times, the costs per unit of time and money are increased. Moreover, the preparation method includes acid-base neutralization reactions, so the process is quite sensitive to the pH value, which causes the viscosity of materials and the blockage of processing pipes. Also, the processing temperature cannot be stably controlled because of the endothermic and exothermic phenomena of the neutralization reactions, such that the operation difficulty is increased over and over again. In addition, in the process of the aforementioned preparation method, the materials have to be moved for several times, which causes risk of pollutions, thereby decreasing the product quality.

[0005] There is a need of providing a preparation method of battery composite material and a precursor thereof to obviate the drawbacks encountered from the prior art.

[0006] CN 101 696 001 A discloses a preparation method for obtaining lithium iron phosphate powder comprising step (a) mixing and stirring 1 mol of phosphoric acid with ferric oxide for 1-4 hours at 20-70 °C under protection of 1-10 L/min of nitrogen gas (N_2); adding the reduced iron power to react for 1-8 hours.

[0007] US 2006 263 286 A discloses a preparation method for lithium batteries comprising step (A) adding iron powder, lithium salt, and phosphate into an acid solution to form a mixture; (B) stirring the mixture; (C) drying the mixture to obtain solid precursor powder; and (D) heating the precursor solid powder at a temperature over 500 °C, to form olivine structured powders.

[0008] US 2008 008 938 A discloses a preparation method for $LiFePO_4/Li_3V_2(PO_4)_3$ composite cathode materials comprising step (A) with reference to $Li_xFe_{1-y}V_yPO_4$, wherein x is between 0.9 and 1.5, and y is between 0 and 1, providing a mixture of iron powder, vanadium, or vanadium compound in a dose ratio to dissolve them into a mixed acid solution (i.e. a mixed acid solution of organic acid and phosphoric acid) to process oxidation reaction. The steps (B) and (C) further disclose: (B) drying the solution in order to obtain precursor powders; and (C) heating the precursor powders at a temperature ranging between 400 and 1000 °C.

BRIEF SUMMARY

[0009] It is an object of the present invention to provide a preparation method of a battery composite material and a precursor thereof in order to eliminate the drawbacks of the high material cost and time cost of preparing the conventional battery, the high sensitivity of pH value of the process caused by neutralization reactions, the blockage of processing pipes, the unstable temperature and the pollutions during movements of materials.

[0010] An object of the present invention provides a preparation method of a battery composite material and a precursor thereof for reducing the grinding time and the costs per unit of time and money in manner of preparing the battery composite material through the precursor produced via reactions. Meanwhile, the sensitivity of pH value of the process is reduced, the viscosity of the material and the blockage of processing pipes are avoided, the processing temperature is stably controlled, and the operation difficulty of the process is reduced.

[0011] Another object of present invention provides a preparation method of a battery composite material and a precursor thereof in order to reduce the waste of materials and totally enhance the product qualities by the fully reacted phosphoric acid and iron powder of the two-times reactions of the phosphoric acid, the deionized water and the iron powder.

[0012] This problem is solved by a preparation method of a battery composite material according to claim 1. Further advantageous embodiments are the subject-matter of the dependent claims. In accordance with an aspect of the present disclosure, there is provided a preparation method of a battery composite material. The preparation method includes steps of providing phosphoric acid, iron powder, a carbon source and a first reactant, allowing deionized water to dissolve a first quantity of said phosphoric acid for forming a first phosphoric acid solution at a first temperature; processing a reaction of said first phosphoric acid solution and said iron powder at a second temperature, lowering the reaction temperature to a third temperature after said second temperature is reached by the reaction temperature, and maintaining the reaction temperature for a first time period; lowering the reaction temperature to a fourth temperature and adding a second phosphoric acid solution consisting a second quantity of said phosphoric acid, and processing a reaction of said first phosphoric acid solution, said second phosphoric acid solution and said iron powder for a second time period in order to produce a first product; calcining the first product to produce a precursor, among which the formula of the precursor is written by $Fe_7(PO_4)_6$, and processing a reaction of the precursor, a third quantity of carbon source and the first reactant to get a reaction mixture and calcining the reaction mixture to produce the battery composite material. The first reactant is a lithium hydroxide, a lithium carbonate, a compound consisting of lithium or a mixture of several compounds consisting of lithium. The first product is an amorphous body of ferric phosphate, and the formula of said first product is written by $a\text{-}FePO_4 \cdot xH_2O$, a stands for amorphous, $x > 0$.

[0013] The above contents of the present disclosure will become more readily apparent to those ordinarily skilled in the art after reviewing the following detailed description and accompanying drawings, in which:

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

FIG. 1 schematically illustrates the flow chart of a preparation method of a battery composite material according to an embodiment of the present invention;

FIG. 2 schematically illustrates a detailed flow chart of the preparation method of a battery composite material according to an embodiment of the present invention;

FIG. 3 schematically illustrates another detailed flow chart of the preparation method of a battery composite material according to an embodiment of the present invention;

FIG. 4 schematically illustrates still another detailed flow chart of the preparation method of a battery composite material according to an embodiment of the present invention;

FIG. 5 schematically illustrates the X-ray diffraction analysis diagram of a precursor prepared by the preparation method of the battery composite material of the present invention;

FIG. 6 schematically illustrates the SEM analysis diagram of the precursor prepared by the preparation method of the battery composite material of the present invention;

FIG. 7 schematically illustrates the X-ray diffraction analysis diagram of the battery composite material prepared by the preparation method of the battery composite material of the present invention;

FIG. 8 schematically illustrates the SEM analysis diagram of the battery composite material prepared by the preparation method of the battery composite material of the present invention; and

FIG. 9 schematically illustrates a charging and discharging characteristic diagram of a cell battery made of the battery composite material prepared by the preparation method of the battery composite material of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0015] The present disclosure will now be described more specifically with reference to the following embodiments. It is to be noted that the following descriptions of preferred embodiments of this disclosure are presented herein for purpose of illustration and description only. It is not intended to be exhaustive or to be limited to the precise form disclosed.

[0016] Please refer to FIG. 1. FIG. 1 schematically illustrates the flow chart of a preparation method of a battery composite material according to an embodiment of the present invention. A preparation method of a batter composite material of the present invention includes steps as follows. At first, providing phosphoric acid, iron powder, a carbon source and a first reactant as shown in step S100, among which the carbon source is not limited to a carbohydrate, an organic compound, a polymer or a macromolecule material, the formula of the phosphoric acid is written by H_3PO_4, and the formula of the iron powder is written by Fe. In some embodiments, the carbohydrate is not limited to fructose, sucrose, lactose or galactose. The macromolecule material is not limited to polyvinylpyrrolidone, and the formula of the macromolecule material is written by $(C_6H_9NO)_n$, among which n is a natural number, and the IUPAC name of the macromolecule material is PVP. The first reactant is lithium hydroxide (LiOH), lithium carbonate (Li_2CO_3), a compound consisting of lithium, or a mixture of several compounds consisting of lithium, but not limited thereto.

[0017] Next, processing a reaction of the phosphoric acid and the iron powder to produce a first product as shown in step S200. In this embodiment, the first product is an amorphous body of ferric phosphate, and the formula of the first product is written by $a\text{-}FePO_4.xH_2O$, among which a > 0 and x > 0.

[0018] Then, adding the carbon source into the reaction of the phosphoric acid and the iron powder, grinding and calcining the first product to produce a precursor as shown in step S300, among which the formula of the precursor is written by $Fe_7(PO_4)_6$.

[0019] Finally, processing a reaction of the precursor and the first reactant to produce the battery composite material as shown in step S400, among which the battery composite material is for example $LiFePO_4$. In the step S400, metal oxide, such as V_2O_5 or MgO, can be added into the reaction, so that a $LiFePO_4$-like material consisting of the metal oxide is produced, which can be called or named "lithium ferric phosphate nano-co-crystalline olivine (LFP-NCO)".

[0020] Under this circumstance, the present invention provides a preparation method of a battery composite material for reducing the material cost in manner of preparing the battery composite material through the precursor produced via reactions and compounds consisting of lithium atom, which is not limited to LiOH. Meanwhile, the sensitivity of pH value of the process is reduced, the viscosity of the material and the blockage of processing pipes are avoided, the processing temperature is stably controlled, and the operation difficulty of the process is reduced.

[0021] Please refer to FIG. 1 and FIG. 2. FIG. 2 schematically illustrates a detailed flow chart of the preparation method of a battery composite material according to an embodiment of the present invention. As shown in FIG. 1 and FIG. 2, the detailed flow chart of the step S200 of the preparation method of the battery composite material of the present invention includes steps as follows. As shown in step S201, allowing deionized water to dissolve a first quantity of the phosphoric acid for forming a first phosphoric acid solution at a first temperature, among which the first temperature can be preheated to a temperature equal to or larger than 40°C and equal to or less than 50°C, and is preferred to be preheated to 42°C, but not limited thereto. Next, as shown in step S202, processing a reaction of the first phosphoric acid solution and the iron powder at a second temperature, lowering the reaction temperature to a third temperature after the second temperature is reached by the reaction temperature, and maintaining the reaction temperature at the third temperature for a first time period. The second temperature is equal to or less than 60°C, and is preferably 60°C, and the third temperature is equal to or less than 50°C, and is preferably 50°C. The first time period is at least 3 hours, and is preferably 3 hours.

[0022] In other words, the preferably embodiment of the step S202 is not limited to be implemented as processing a reaction of the first phosphoric acid solution and the iron powder at 60°C, lowering the reaction temperature to 50°C after the reaction temperature reached 60°C, and maintaining the reaction temperature at 50°C for 3 hours. Then, as shown in step S203, lowering the reaction temperature to a fourth temperature and adding a second phosphoric acid solution consisting a second quantity of the phosphoric acid, and processing a reaction of the first phosphoric acid solution, the second phosphoric acid solution and the iron powder for a second time period in order to produce the first product.

[0023] In this embodiment, the first product is an amorphous body of ferric phosphate, and the formula of the first product is written by a-FePO4·xH_2O (a>=, x>0). The fourth temperature is equal to or less than 30°C, and is preferably 30°C. The second time period is at least 23 hours, and is preferably 23 hours. The weight ratio of the first quantity to the second quantity is 3:1, i.e. the first quantity is 75% and the second quantity is 25%. Via the fully reacted phosphoric acid and iron powder of the two-times reactions of the phosphoric acid, the deionized water and the iron powder, the waste of materials is reduced, and the product qualities are totally enhanced.

[0024] After 26 hours of the above-mentioned reaction, the step S300 of the preparation method of the battery composite material of the present invention is performed. Please refer to FIG. 3. FIG. 3 schematically illustrates another detailed flow chart of the preparation method of a battery composite material according to an embodiment of the present invention. At first, as shown in step S301 illustrated in FIG. 3, grinding the first product at a first rotational speed, among which the first rotational speed is equal to or greater than 450 rpm and equal to or less than 650 rpm, and is preferably 550 rpm.

[0025] Next, as shown in step S302, adding the carbon source, such as the macromolecule material PVP, after the first product is grinded for a third time period, which is preferably at least 5 minutes, processing a reaction of the macromolecule material and the first product to produce a precursor solution, and continuously performing the grinding till the step S303. The step S303 is shown as performing a spray drying action and a thermal treatment to the precursor solution in order to obtain the precursor when the average diameter of particles (i.e. particle size distribution D50) of the precursor solution is grinded so as to be less than a first length, among which the first length is for example but not limited to 1 micrometer. The formula of the precursor is written by $Fe_7(PO4)_6$.

[0026] In this embodiment, the spray drying action is implemented by a rotary spray dryer. An entrance temperature of the spray drying action or the rotary spray dryer is 210°C, an exit temperature of the spray drying action or the rotary spray dryer is -95°C, and the rotational speed of the spray drying action or the rotary spray dryer is 350 Hz, but not limited thereto. On the other hand, the thermal treatment is sequentially performed at 280°C for 2 hours and at 350°C for 1 hour in helium atmosphere.

[0027] The precursor of the preparation method of the battery composite material of the present invention is completely prepared. The detailed flow char of the step S400 is described as follows. Please refer to FIG. 4. FIG. 4 schematically illustrates still another detailed flow chart of the preparation method of a battery composite material according to an embodiment of the present invention. As shown in FIG. 4, the detailed flow chart of the step S400 includes steps of mixing the precursor (i.e. $Fe_7(PO_4)_6$) and the first reactant, which is not limited to be a compound consisting of lithium such as LiOH or Li_2CO_3, or a mixture of several compounds consisting of lithium, as shown in step S401, adding a dispersant and performing a spray granulation as shown in step S402, performing a high-temperature calcination as shown in step S403, and producing the battery composite material, which is for example lithium ferric phosphate (i.e. $LiFePO_4$), as shown in step S404.

[0028] The following embodiment is presented herein for purpose of illustration and description of the preparation method of the battery composite material of the present disclosure.

Embodiment

[0029] At first, providing 5169 grams of phosphoric acid (Purity>85%), 12.2 liters of deionized water and 2948 grams of iron powder (Purity>99%) and processing two-times reactions and stirring for 26 hours. Next, adding a dispersant and using a horizontal sander to grind the mixture (450~650rpm) for 1 hour, among which a carbon source (e.g. a carbohydrate, an organic compound, a polymer or a macromolecule material such as PVP) is added in this step, to obtain a $Fe_7(PO_4)_6$ precursor solution. Then, performing a spray drying action to the precursor solution, putting the product into a ceramic sagger, and performing a calcination to the product, among which the calcination is sequentially performed at 280°C for 2 hours and at 350°C for 1 hour in helium atmosphere. The calcined compound is analyzed in manner of X-ray diffraction, and the analysis diagram is shown as FIG. 5. After comparing the diagram with JCPDS card, the compound is confirmed to be $Fe_7(PO_4)_6$. The surface exterior is analyzed through SEM, and the SEM analysis diagram is shown as FIG. 6.

[0030] Next, adding 4804 grams of $Fe_7(PO_4)_6$ obtained in the above-mentioned steps, 392 grams of phosphoric acid, 189 grams of lithium carbonate, 3.5 grams of vanadium pentoxide, 62.5 grams of fructose and 0.06 grams of TritonX-100® into pure water for grinding of the horizontal sander. After grinding, the $LiFePO_4$ precursor solution is obtained. Then, performing a spray drying action to this precursor solution, putting the product into a ceramic sagger, and performing a calcination to the product, among which the calcination is performed at 550°C to 750°C for 8 to 12 hours in nitrogen atmosphere. The calcined compound is analyzed in manner of X-ray diffraction, and the analysis diagram is shown as FIG. 7. After comparing the diagram with JCPDS card, the compound is confirmed to be $LiFePO_4$. The surface exterior is analyzed through SEM, and the SEM analysis diagram is shown as FIG. 8.

[0031] A coin-cell battery is made of the $LiFePO_4$ obtained in this embodiment. The electric characteristics of charging and discharging are tested and analyzed through a charging and discharging machine. The test and the analysis are performed at 0.1 coulombs for two cycles and 2 coulombs for two cycles. The charging and discharging characteristic diagram is shown as FIG. 9. The cutoff voltage of the coin-cell battery is 2 to 4.2 volts.

[0032] From the above description, the present invention provides a preparation method of a battery composite material and a precursor thereof for reducing the grinding time and the costs per unit of time and money in manner of preparing the battery composite material through the precursor produced via reactions. Meanwhile, the sensitivity of pH value of the process is reduced, the viscosity of the material and the blockage of processing pipes are avoided, the processing temperature is stably controlled, and the operation difficulty of the process is reduced. Additionally, the present disclosure also provides a preparation method of a battery composite material and a precursor thereof in order to reduce the waste of materials and totally enhance the product qualities by the fully reacted phosphoric acid and iron powder of the two-times reactions of the phosphoric acid, the deionized water and the iron powder.

Claims

1. A preparation method of a battery composite material, comprising steps of:

(a) providing phosphoric acid, iron powder, a carbon source and a first reactant;

(b1) allowing deionized water to dissolve a first quantity of said phosphoric acid for forming a first phosphoric acid solution at a first temperature;
(b2) processing a reaction of said first phosphoric acid solution and said iron powder at a second temperature, lowering the reaction temperature to a third temperature after said second temperature is reached by the reaction temperature, and maintaining the reaction temperature for a first time period; and
(b3) lowering the reaction temperature to a fourth temperature and adding a second phosphoric acid solution consisting of a second quantity of phosphoric acid, and processing a reaction of said first phosphoric acid solution, said second phosphoric acid solution and said iron powder for a second time period in order to produce a first product,

(c) adding said carbon source, grinding and calcining said first product to produce a precursor, wherein the formula of said precursor is written

by $Fe_7(PO_4)_6$; and
(d) processing a reaction of said precursor and said first reactant to obtain a reaction mixture, and then calcining said reaction mixture to produce said battery composite material,

wherein said first reactant is a lithium hydroxide, a lithium carbonate, a compound consisting of lithium or a mixture of several compounds consisting of lithium,
said first product is an amorphous body of ferric phosphate, and the formula of said first product is written by a-$FePO_4 \cdot xH_2O$, wherein a > 0 and x > 0.

2. The preparation method according to claim 1, wherein said carbon source is a carbohydrate, an organic compound, a polymer or a macromolecule material, and wherein said macromolecule material is polyvinylpyrrolidone, and the formula of said macromolecule material is written by $(C_6H_9NO)_n$, wherein n is a natural number, and the IUPAC name of said macromolecule material is PVP.

3. The preparation method according to claim 1, wherein said first reactant is a lithium carbonate, and the formula of said first reactant is written by Li_2CO_3, and wherein said battery composite material is a lithium ferric phosphate nano-co-crystalline olivine (LFP-NCO).

4. The preparation method according to claim 1, wherein the weight ratio of said first quantity to said second quantity is 3:1.

5. The preparation method according to claim 1, wherein said first temperature is equal to or larger than 40°C and equal to or less than 50°C, said second temperature is equal to or less than 60°C, said third temperature is equal to or less than 50°C, and said fourth temperature is equal to or less than 30°C.

6. The preparation method according to claim 1, wherein said first time period is at least 3 hours and said second time period is at least 23 hours.

7. The preparation method according to claim 1, wherein said carbon source is a macromolecule material, and wherein said step (c) further comprises steps of:

(c1) grinding said first product at a first rotational speed;
(c2) adding said macromolecule material after said first product is grinded for a third time period, processing a reaction of said macromolecule material and said first product to produce a precursor solution, and continuously performing the grinding; and
(c3) performing a spray drying action and a thermal treatment to said precursor solution in order to obtain said precursor when the average diameter of particles of said precursor solution is grinded so as to be less than a first length.

8. The preparation method according to claim 7, wherein an entrance temperature of said spray drying action is 210°C, an exit temperature of said spray drying action is -95°C, and the rotational speed of said spray drying action is 350 Hz.

9. The preparation method according to claim 7, wherein said thermal treatment is sequentially performed at 280°C for 2 hours and at 350°C for 1 hour in helium atmosphere.

10. The preparation method according to claim 7, wherein said first rotational speed is equal to or greater than 450 rpm and equal to or less than 650 rpm.

11. The preparation method according to claim 7, wherein said third time period is at least 5 minutes.

12. The preparation method according to claim7, wherein said first length is 1 micrometer.

13. The preparation method according to claim 1, wherein said step (d) further comprises steps of:

(d1) mixing said precursor and said first reactant;
(d2) adding a dispersant and performing a spray granulation;
(d3) performing a high-temperature calcination; and
(d4) producing said battery composite material.

Patentansprüche

1. Herstellungsverfahren für ein Batterieverbundmaterial, umfassend die Schritte:

(a) Bereitstellen von Phosphorsäure, Eisenpulver, einer Kohlenstoffquelle und einem ersten Reaktionspartner;

(b1) Deionisiertes Wasser eine erste Menge der Phosphorsäure lösen zu lassen, um eine erste Phosphorsäurelösung bei einer ersten Temperatur zu bilden;
(b2) Durchführen einer Reaktion der ersten Phosphorsäurelösung und des Eisenpulvers bei einer zweiten Temperatur, Absenken der Reaktionstemperatur auf eine dritte Temperatur, nachdem die zweite Temperatur durch die Reaktionstemperatur erreicht ist, und Halten der Reaktionstemperatur für

eine erste Zeitspanne; und

(b3) Absenken der Reaktionstemperatur auf eine vierte Temperatur und Zugabe einer zweiten Phosphorsäurelösung, die aus einer zweiten Menge Phosphorsäure besteht, und Verarbeiten einer Reaktion der ersten Phosphorsäurelösung, der zweiten Phosphorsäurelösung und des Eisenpulvers für einen zweiten Zeitraum, um ein erstes Produkt herzustellen,

(c) Hinzufügen der Kohlenstoffquelle, Mahlen und Kalzinieren des ersten Produkts, um einen Vorläufer herzustellen, wobei die Formel des Vorläufers durch $Fe7(PO4)_6$ beschrieben ist; und

(d) Durchführen einer Reaktion des Vorläufers und des ersten Reaktanten, um ein Reaktionsgemisch zu erhalten, und dann Kalzinieren des Reaktionsgemischs, um das Batterieverbundmaterial herzustellen,

wobei der erste Reaktant ein Lithiumhydroxid, ein Lithiumcarbonat, eine Verbindung, bestehend aus Lithium, oder eine Mischung aus mehreren Verbindungen, bestehend aus Lithium, ist,
das erste Produkt ein amorpher Körper aus Eisen(III)-Phosphat ist, und die Formel des ersten Produkts durch a-FePO4 • xH2O beschrieben ist, wobei a > 0 und x > 0.

2. Herstellungsverfahren nach Anspruch 1, wobei die Kohlenstoffquelle ein Kohlenhydrat, eine organische Verbindung, ein Polymer oder ein Makromolekülmaterial ist, und wobei das Makromolekülmaterial Polyvinylpyrrolidon ist und die Formel des Makromolekülmaterials durch $(C_6H_9NO)_n$ beschrieben ist, wobei n eine natürliche Zahl ist und der IUPAC-Name des Makromolekülmaterials PVP ist.

3. Herstellungsverfahren nach Anspruch 1, wobei der erste Reaktant ein Lithiumcarbonat ist und die Formel des ersten Reaktanten durch Li_2CO_3 beschrieben ist, und wobei das Batterieverbundmaterial ein Lithiumferritphosphat-Nanokristallines Olivin (LFP-NCO) ist.

4. Herstellungsverfahren nach Anspruch 1, wobei das Gewichtsverhältnis der ersten Menge zu der zweiten Menge 3:1 beträgt.

5. Herstellungsverfahren nach Anspruch 1, wobei die erste Temperatur gleich oder größer als 40°C und gleich oder kleiner als 50°C ist, die zweite Temperatur gleich oder kleiner als 60°C ist, die dritte Temperatur gleich oder kleiner als 50°C ist und die vierte Temperatur gleich oder kleiner als 30°C ist.

6. Herstellungsverfahren nach Anspruch 1, wobei die erste Zeitspanne mindestens 3 Stunden und die zweite Zeitspanne mindestens 23 Stunden beträgt.

7. Herstellungsverfahren nach Anspruch 1, wobei die Kohlenstoffquelle ein Makromolekülmaterial ist, und wobei der Schritt (c) ferner die Schritte umfasst:

(c1) Mahlen des ersten Produkts bei einer ersten Drehzahl;

(c2) Hinzufügen des Makromolekülmaterials, nachdem das erste Produkt für einen dritten Zeitraum gemahlen wurde, Verarbeiten einer Reaktion des Makromolekülmaterials und des ersten Produkts, um eine Vorläuferlösung herzustellen, und kontinuierliches Durchführen der Vermahlung; und

(c3) Durchführen einer Sprühtrocknung und einer Wärmebehandlung der Vorläuferlösung, um den Vorläufer zu erhalten, wenn der durchschnittliche Durchmesser der Partikel der Vorläuferlösung gemahlen wird, so dass er kleiner als eine erste Länge ist.

8. Herstellungsverfahren nach Anspruch 7, wobei eine Eintrittstemperatur der Sprühtrocknung 210°C, eine Austrittstemperatur der Sprühtrocknung -95°C und die Drehgeschwindigkeit der Sprühtrocknung 350 Hz beträgt.

9. Herstellungsverfahren nach Anspruch 7, wobei die Wärmebehandlung nacheinander bei 280°C für 2 Stunden und bei 350°C für 1 Stunde in Heliumatmosphäre durchgeführt wird.

10. Herstellungsverfahren nach Anspruch 7, wobei die erste Drehzahl gleich oder größer als 450 U/min und gleich oder kleiner als 650 U/min ist.

11. Herstellungsverfahren nach Anspruch 7, wobei die dritte Zeitspanne mindestens 5 Minuten beträgt.

12. Herstellungsverfahren nach Anspruch 7, wobei die erste Länge 1 Mikrometer beträgt.

13. Herstellungsverfahren nach Anspruch 1, wobei der Schritt (d) ferner die Schritte umfasst:

(d1) Mischen des Vorläufers und des ersten Reaktanten;

(d2) Zugabe eines Dispersionsmittels und Durchführung einer Sprühgranulation;

(d3) Durchführen einer Hochtemperaturkalzinierung; und

(d4) Herstellen des Batterieverbundmaterials.

Revendications

1. Procédé de préparation d'un matériau composite de batterie, comprenant les étapes consistant à :

(a) se procurer de l'acide phosphorique, de la poudre de fer, une source de carbone et un premier réactif ;

(b1) amener de l'eau déionisée à dissoudre une première quantité dudit acide phosphorique pour former une première solution d'acide phosphorique à une première température ;

(b2) faire réagir ladite première solution d'acide phosphorique et ladite poudre de fer à une deuxième température, abaisser la température de réaction à une troisième température après que ladite deuxième température est atteinte par la température de réaction et maintenir la température de réaction pendant une première période de temps ; et

(b3) abaisser la température de réaction à une quatrième température et ajouter une seconde solution d'acide phosphorique consistant en une seconde quantité d'acide phosphorique et faire réagir ladite première solution d'acide phosphorique, ladite seconde solution d'acide phosphorique et ladite poudre de fer pendant une deuxième période de temps afin de produire un premier produit ;

(c) ajouter ladite source de carbone, broyer et calciner ledit premier produit pour produire un précurseur, la formule dudit précurseur étant écrite par $Fe_7(PO_4)_6$; et

(d) faire réagir ledit précurseur et ledit premier réactif pour obtenir un mélange réactionnel, puis calciner ledit mélange réactionnel pour produire ledit matériau composite de batterie,

dans lequel ledit premier réactif est un hydroxyde de lithium, un carbonate de lithium, un composé du lithium ou un mélange de plusieurs composés du lithium,
ledit premier produit est un corps amorphe de phosphate ferrique et la formule dudit premier produit est écrite par $a\text{-}FePO_4 \cdot xH_2O$, où $a > 0$ et $x > 0$.

2. Procédé de préparation selon la revendication 1, dans lequel ladite source de carbone est un glucide, un composé organique, un polymère ou une matière macromoléculaire et dans lequel ladite matière macromoléculaire est la polyvinylpyrrolidone et la formule de ladite matière macromoléculaire est écrite par $(C_6HgNO)_n$, où n est un nombre naturel et la dénomination IUPAC de ladite matière macromoléculaire est PVP.

3. Procédé de préparation selon la revendication 1, dans lequel ledit premier réactif est un carbonate de lithium et la formule dudit premier réactif est écrite par Li_2CO_3, et dans lequel ledit matériau composite de batterie est une olivine nano-co-cristalline de lithium phosphate ferrique (LFP-NCO).

4. Procédé de préparation selon la revendication 1, dans lequel le rapport en poids de ladite première quantité à ladite seconde quantité est de 3:1.

5. Procédé de préparation selon la revendication 1, dans lequel ladite première température est égale ou supérieure à 40°C et égale ou inférieure à 50°C, ladite deuxième température est égale ou inférieure à 60°C, ladite troisième température est égale ou inférieure à 50°C et ladite quatrième température est égale ou inférieure à 30°C.

6. Procédé de préparation selon la revendication 1, dans lequel ladite première période de temps est d'au moins 3 heures et ladite deuxième période de temps est d'au moins 23 heures.

7. Procédé de préparation selon la revendication 1, dans lequel ladite source de carbone est une matière macromoléculaire, et dans lequel ladite étape (c) comprend en outre les étapes consistant à :

(c1) broyer ledit premier produit à une première vitesse de rotation ;

(c2) ajouter ladite matière macromoléculaire après que ledit premier produit est broyé pendant une troisième période de temps, faire réagir ladite matière macromoléculaire et ledit premier produit pour produire une solution de précurseur et effectuer en continu le broyage ; et

(c3) effectuer une action de séchage par pulvérisation et un traitement thermique sur ladite solution de précurseur afin d'obtenir ledit précurseur lorsque le diamètre moyen des particules de ladite solution de précurseur est broyé de façon à être inférieur à une première longueur.

8. Procédé de préparation selon la revendication 7, dans lequel une température d'entrée de ladite action de séchage par pulvérisation est de 210°C, une température de sortie de ladite action de séchage par pulvérisation est de -95°C et la vitesse de rotation de ladite action de séchage par pulvérisation est de 350 Hz.

9. Procédé de préparation selon la revendication 7, dans lequel ledit traitement thermique est effectué séquentiellement à 280°C pendant 2 heures et à

350°C pendant 1 heure dans une atmosphère d'hélium.

10. Procédé de préparation selon la revendication 7, dans lequel ladite première vitesse de rotation est égale ou supérieure à 450 tpm et égale ou inférieure à 650 tpm.

11. Procédé de préparation selon la revendication 7, dans lequel ladite troisième période de temps est d'au moins 5 minutes.

12. Procédé de préparation selon la revendication 7, dans lequel ladite première longueur est de 1 micromètre.

13. Procédé de préparation selon la revendication 1, dans lequel ladite étape (d) comprend en outre les étapes consistant à :

(d1) mélanger ledit précurseur et ledit premier réactif ;
(d2) ajouter un dispersant et effectuer une granulation par pulvérisation ;
(d3) effectuer une calcination à haute température ; et
(d4) produire ledit matériau composite de batterie.

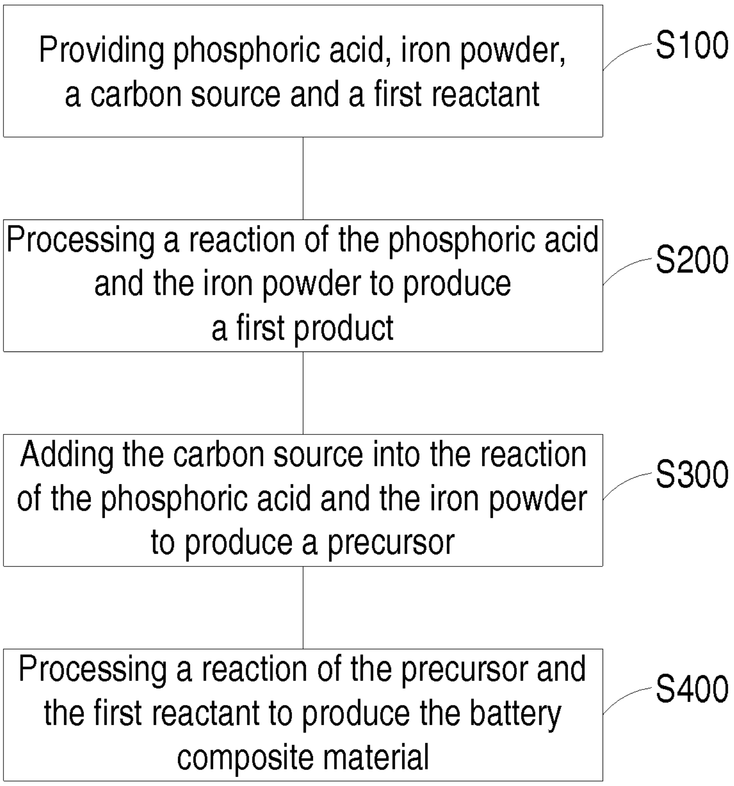
Providing phosphoric acid, iron powder, a carbon source and a first reactant
S100
Processing a reaction of the phosphoric acid and the iron powder to produce a first product
S200
Adding the carbon source into the reaction of the phosphoric acid and the iron powder to produce a precursor
S300
Processing a reaction of the precursor and the first reactant to produce the battery composite material
S400

FIG. 1

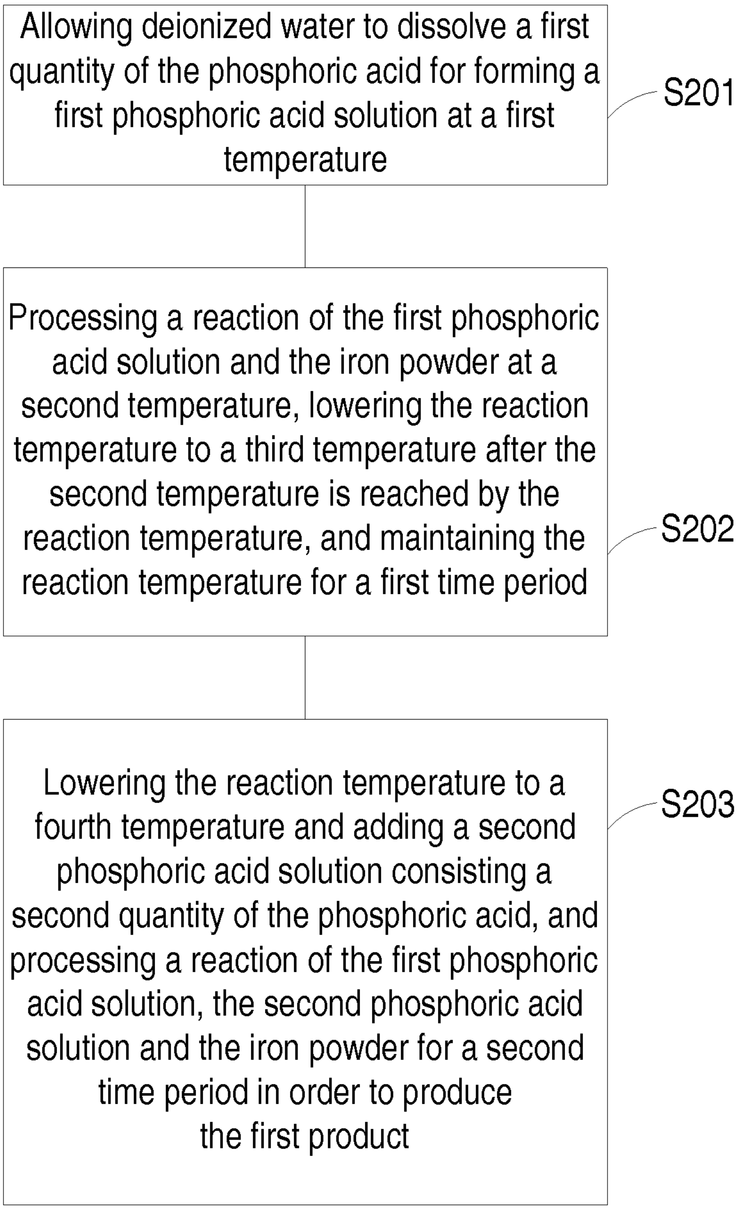
Allowing deionized water to dissolve a first quantity of the phosphoric acid for forming a first phosphoric acid solution at a first temperature
S201
Processing a reaction of the first phosphoric acid solution and the iron powder at a second temperature, lowering the reaction temperature to a third temperature after the second temperature is reached by the reaction temperature, and maintaining the reaction temperature for a first time period
S202
Lowering the reaction temperature to a fourth temperature and adding a second phosphoric acid solution consisting a second quantity of the phosphoric acid, and processing a reaction of the first phosphoric acid solution, the second phosphoric acid solution and the iron powder for a second time period in order to produce the first product
S203

FIG. 2

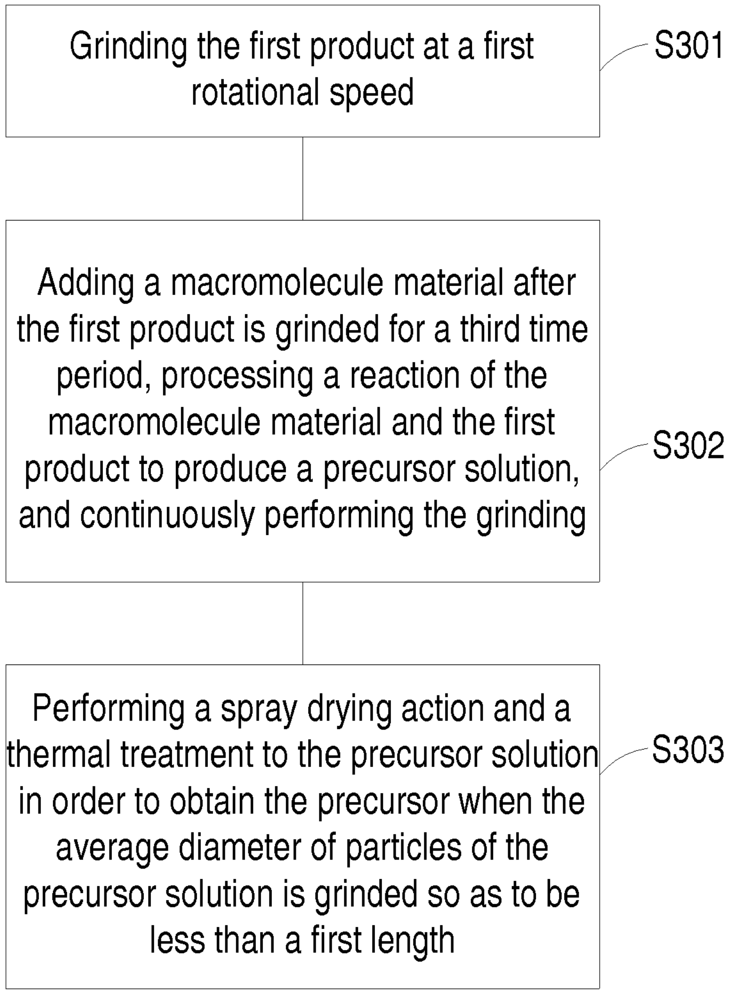
Grinding the first product at a first rotational speed
S301
Adding a macromolecule material after the first product is grinded for a third time period, processing a reaction of the macromolecule material and the first product to produce a precursor solution, and continuously performing the grinding
S302
Performing a spray drying action and a thermal treatment to the precursor solution in order to obtain the precursor when the average diameter of particles of the precursor solution is grinded so as to be less than a first length
S303

FIG. 3

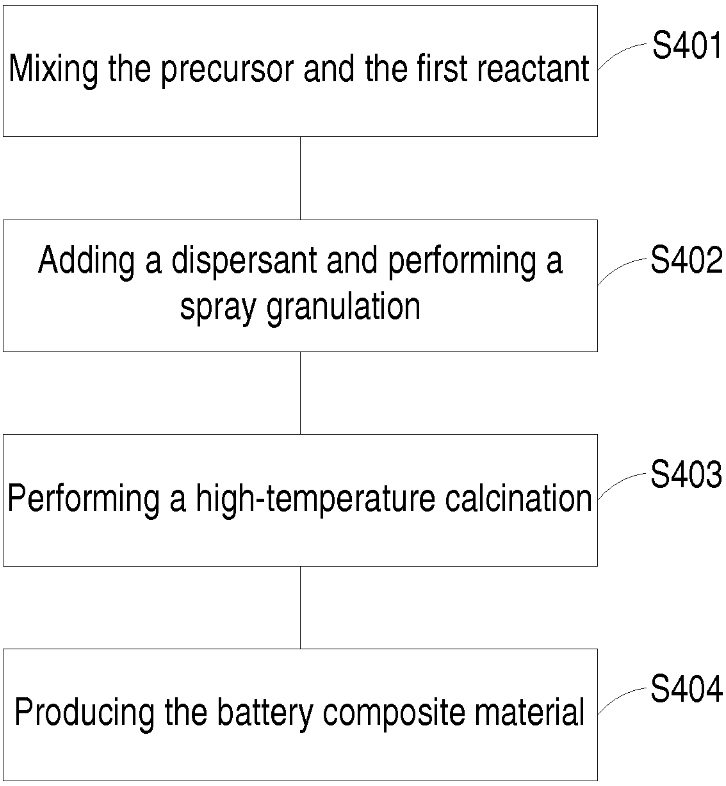
Mixing the precursor and the first reactant
S401
Adding a dispersant and performing a spray granulation
S402
Performing a high-temperature calcination
S403
Producing the battery composite material
S404

FIG. 4

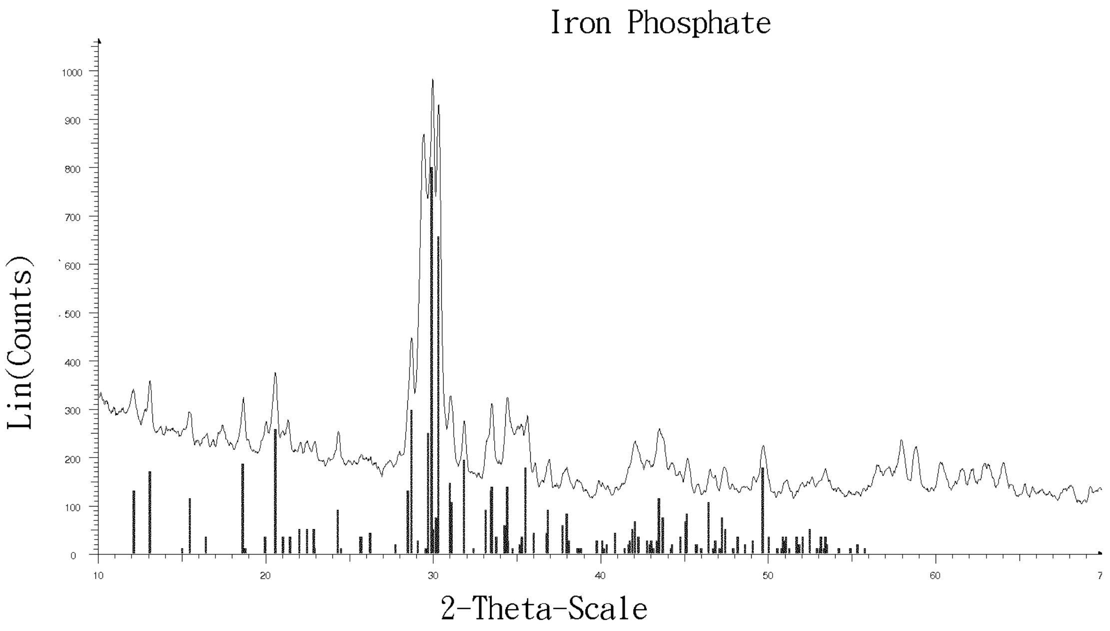
Iron Phosphate
Lin(Counts)
1000
900
800
700
600
500
400
300
200
100
0
10
20
30
40
50
60
7
2-Theta-Scale

FIG. 5

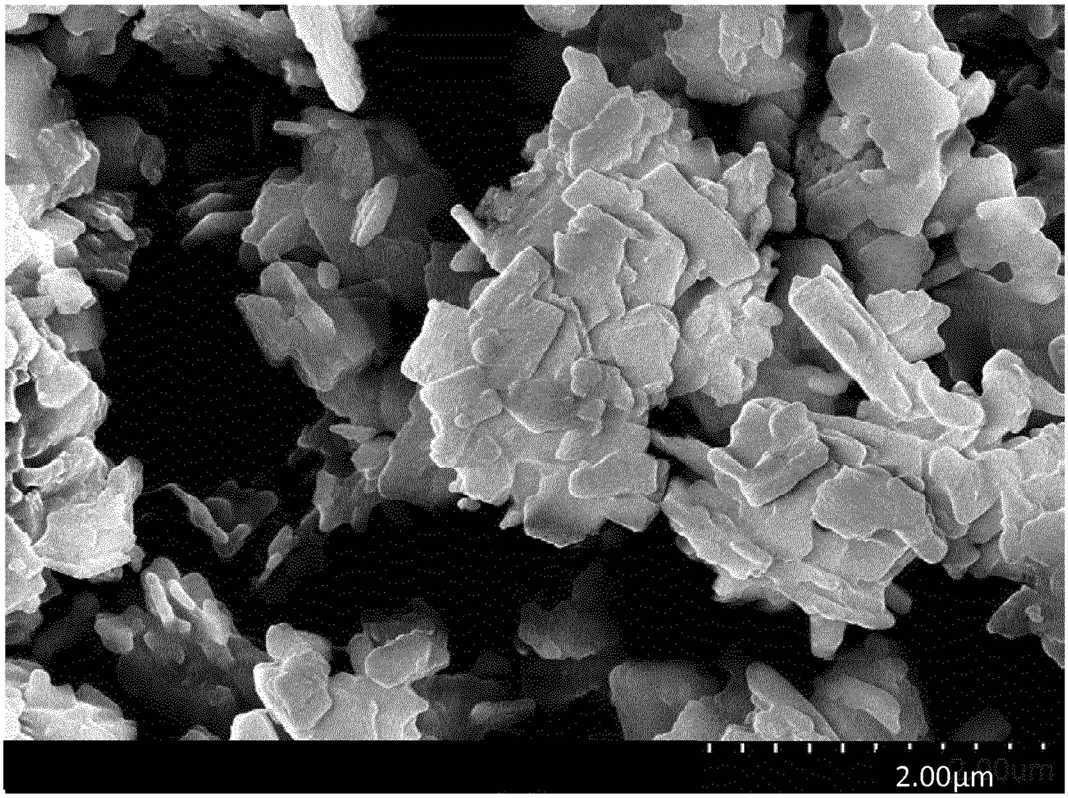
2.00µm

FIG. 6

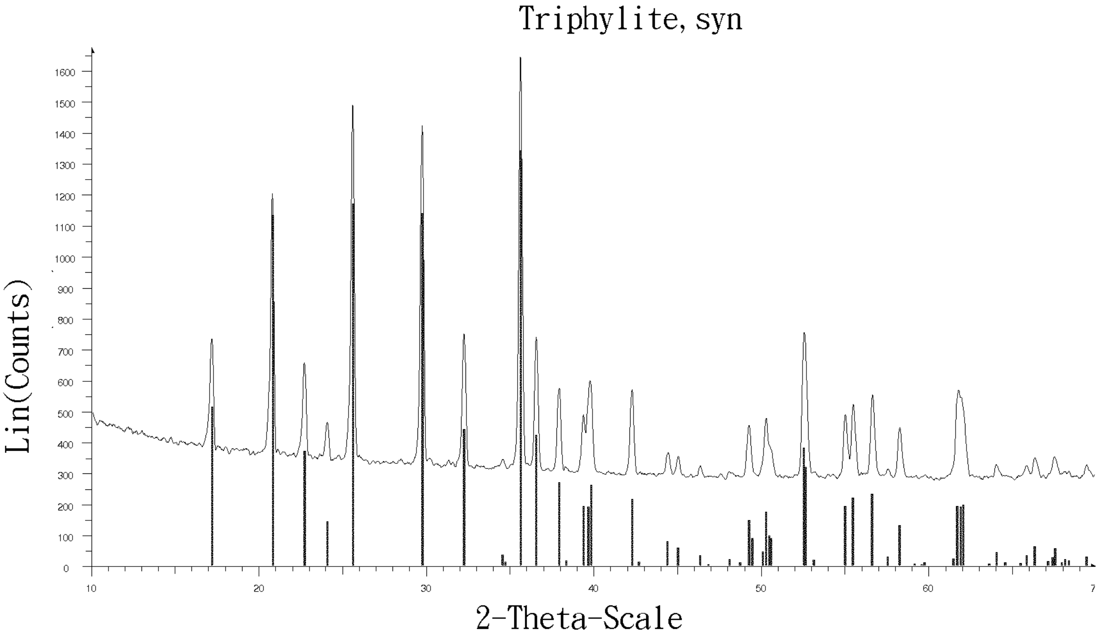
Triphylite, syn
Lin(Counts)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
10
20
30
40
50
60
7
2-Theta-Scale

FIG. 7

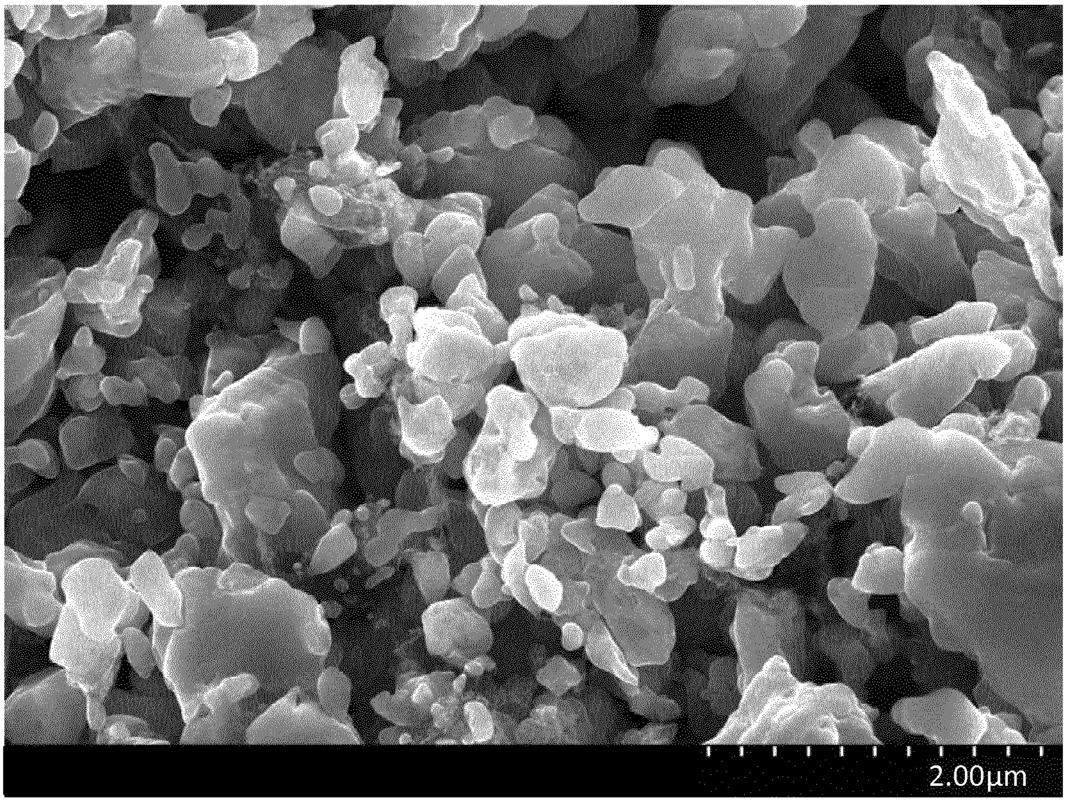
2.00μm

FIG. 8


Voltage
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
mAh/g
0
20
40
60
80
100
120
140
160
1st charge 159mAh/g
1st discharge 159mAh/g
2nd charge 153mAh/g
2nd discharge 153mAh/g
3rd charge 152mAh/g
3rd discharge 115mAh/g
4th charge 114mAh/g
4th discharge 113mAh/g

FIG. 9

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- CN 101696001 A **[0006]**
- US 2006263286 A **[0007]**
- US 2008008938 A **[0008]**